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Tuning Charge Transfer in Ion-Surface Collisions at Hyperthermal Energies**

*Yunxi Yao and Konstantinos P. Giapis**

Abstract:Charge exchange in ion-surface collisions may be influenced by surface adsorbates to alter the charge state of the scattered projectiles. We show here that the positive ion yield, observed during ion scattering on metal surfaces at low incident energies, is greatly enhanced by adsorbing electronegative species onto the surface. Specifically, when beams of N^+ and O^+ ions are scattered off on clean Au surfaces at hyperthermal energies, no positive ions are observed exiting. Partial adsorption of F atoms on the Au surface, however, leads to the appearance of positively charged primary ions scattering off of Au, a direct result of the increase in the Au work function. The inelastic energy losses for positive ion exits are slightly larger than the corresponding ionization energies of the respective N and O atoms, which suggests that the detected positive ions are formed by surface re-ionization during the hard collision event.

Charge transfer in ion-surface collisions is of fundamental importance to surface dynamics.[1] Determining and influencing the charge state of scattered products is also of practical significance. For example, whether ions scatter as neutral or charged projectiles can have significant impact on profile evolution during plasma etching of semiconductor devices because the trajectories of charged species will be influenced by pattern charging.[2] Surface neutralization and re-ionization are also essential processes for analytical techniques such as Low-Energy Ion Scattering (LEIS) spectroscopy and Surface-Induced Dissociation (SID), which rely on detecting primary projectiles and/or their fragments after interacting energetically with surface atoms.[3-4] These methods generally employ low-energy ions, which are efficiently neutralized near good metal surfaces, making it particularly difficult to detect scattering products. Low-energy ion-surface collisions are also important in a variety of reactive processes at surfaces such as electron transfer reactions, atom abstraction, and oxidation.

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In contrast to charge transfer in ion-surface collisions at high impact energies (keV-range),[5-6] scattering at lower impact energies (≤200 eV) has received much less attention. The reason is simple: high incident energies guarantee the formation of positive primary exits through electronic promotions in neutralized projectiles or through ion survival, even on good metal surfaces. Low incident energies, however, generally suffer from extremely low ion scattering yield,[7] which frequently prevents reliable charge and energy transfer measurements.[8] Controlling the charge state of primary projectiles after they undergo surface scattering and, ultimately, increasing ion yield is imperative for surface dynamics, especially in the "hyperthermal" energy regime (10-200 eV).

Charge transfer on surfaces is very sensitive to surface contamination.[9] In such studies, impurities must be painstakingly detected and removed from surfaces so as not to alter the charge state of the scattered projectiles.[9] In the other extreme, adsorbing alkali impurities onto surfaces has been purposely used to drastically increase the yield of scattered negative primary ions.[10-11] This effect has been attributed to the strong reduction in the metal surface work-function induced by the adsorbates, though the local modification in the surface electronic structure has been implicated as well, especially at short atom-surface distances achieved at high collision energies. When no ions are scattered off, the adsorbate effect permits an assessment of the scattering dynamics by looking at negative primaries. However, such a study may be incomplete without detecting positive primaries, whose formation involves different inelastic energy loss mechanisms at the surface. Positive primary ion exits are typically not a problem at high collision energies (>2 keV), but the signal weakens dramatically when the incident energy decreases below 300eV. A question arises, then, whether electronegative adsorbates may be used to increase the work function of the metal surface so that the appearance of positive ion primaries may be enhanced. Electronegative adsorbates have been shown to reduce negative ion yields, as expected from the reverse sign of the adsorbate dipole.[12] However, their effect on positive ion yields has not been demonstrated in ion-surface scattering experiments at low incident energies.

Here we study the positive and negative ion yields of N^+ and O^+ ion-beams scattering off polycrystalline Au foils as a function of the degree of fluorination of the surface. We focus on primary ion scattering from single-collision events with surface Au atoms. Such scattered primaries are easily discriminated in an exit energy spectrum against sputtered surface species by peaks whose energy depends linearly on the incident energy. N^+ ion bombardment of clean Au surfaces at hyperthermal energies produces no detectable scattered ions, positive or negative. Adsorbing F atoms on the Au surface, however, produces strong N^+ scattering signal, thus enabling the study of the relevant surface dynamics. For O^+ ion scattering off of a clean Au surface, O^- is exclusively observed exiting the surface: no scattered O^+ is detected. Upon fluorination of the Au surface, however, *both* O^- and O^+ ion exits are detected. Then, the kinematics of O^- and O^+ ion exits can

be compared, permitting an evaluation of the mechanisms for O^+ and O^- formation and, thus, offering deeper insight into the surface scattering dynamics.

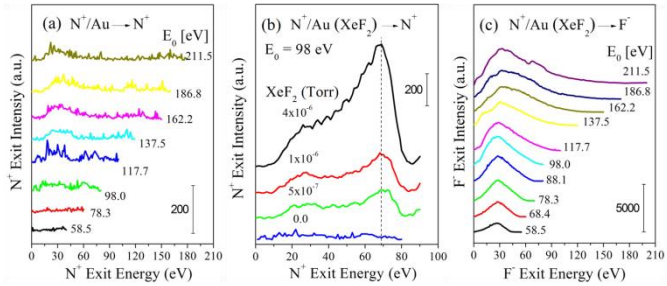

Figure 1. (a) Energy distributions of N^+ ion exits from N^+ scattering on clean Au at various incident beam energies (E_0). Only weak N^+ sputtering signal is seen for E_0 >100 eV. (b) Energy distributions of N^+ ion exits for N^+ scattering on Au exposed to XeF_2 at various background pressures (E_0=98 eV). Elastically scattered N^+ is observed at exit energy of ~70 eV. (c) Energy distributions of F- ion exits from N^+ scattering on Au exposed to a background of 3×10^{-6} Torr XeF_2 at various E_0. Strong F^- sputtering signal is observed at an exit energy of ~30 eV, confirming an F covered Au surface.

Figure 1a shows N^+ scattering data from experiments on a clean Au surface, normalized by the corresponding beam current at each incident energy. No N^+ scattering signal is detected at incident energies below ~100 eV. Above that energy, only a weak and noisy N^+ peak is observed, centered around 30 eV, due to sputtering. Negative ion exits have not been detected for N^+ scattering on any high work function metal surfaces (e.g., Au, Pt, Pd), despite the very sensitive detection limits of the apparatus. Thus, it appears that all incident N^+ ions become neutralized, probably due to very efficient Auger capture of two electrons from the Au surface.[13] A study of the ion-surface dynamics for the N^+/Au system is then impossible without additional effort to spectroscopically detect or re-ionize the neutralized projectiles.

Adsorbing F atoms onto the Au surface is expected to cause an increase in the surface work function, similar to Cl adsorption on Au[14]. This, in turn, should influence significantly the charged state of the scattered N projectiles. Fluorination of the surface is accomplished during the N^+ ion scattering experiment by introducing XeF_2 gas directly onto the Au foil with a doser pipe situated ~2 cm from the surface. XeF_2 adsorbs dissociatively onto metal surfaces,[15-17] thus providing a convenient way to change the F-atom surface coverage by controlling the XeF_2 background gas pressure. Though not measured, fluorine coverage is kept sub-monolayer by limiting the background pressure below the point where the scattered signal saturates. Representative scattering results as a function of XeF_2 pressure are shown in Figure 1b. As mentioned before, there is no discernible N^+ scattering signal when an N^+ beam is directed onto a clean Au surface at an incident energy of 98±5 eV. Upon exposure to XeF_2 gas at a background pressure of 5×10^{-7} Torr, an N^+ scattering peak appears, centered at ~70 eV. Simultaneously, a weaker N^+ sputtering peak becomes discernible around 30 eV. Increasing the XeF_2 background pressure causes both N^+ scattering and sputtering peaks to become more pronounced. At a pressure of 4×10^{-6} Torr, the effect is disproportionally larger for the N^+ scattering peak. The presence of surface F was confirmed by the appearance of an F^- sputtering peak at an exit energy of ~30 eV for all XeF_2 exposures, also produced by the N^+ beam (see Figure 1c).

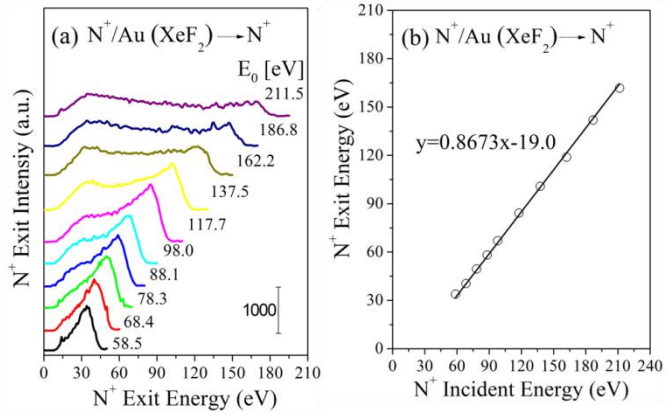

Figure 2. (a) Energy distributions of N^+ ion exits during N^+ scattering on Au in a background of 3×10^{-6} Torr XeF_2 at various incident energies. (b) Peak N^+ ion exit energy as a function of incident beam energy. The linear fitting is performed with a fixed slope of 0.8673, corresponding to the BCA-calculated kinematic factor for N^+/Au at a deflection angle of 90°.

The appearance of a strong N^+ scattering peak, following the partial fluorination of the Au surface, enables the study of the scattering dynamics of N^+ on Au. Beams of N^+ ions at variable incident energy (E_0) were scattered off of a Au surface exposed to a background of 3×10^{-6} Torr XeF_2. Energy distributions of N^+ exits as a function of the incident energy are shown in Figure 2a. The scattered N^+ exit energy, corresponding to the peak in the collected energy distribution, depends linearly on the incident beam energy (see Figure 2b), in agreement with the binary collision approximation (BCA).[5] In fact, the slope of the linear fit shown in Figure 2b is the kinematic factor of 0.8673 predicted by BCA for N^+/Au at a deflection angle of 90°. This result confirms that the observed scattering signal originates from single-collision events with individual Au atoms. The linear fitting yields an intercept of -19.0 eV, which corresponds to the cumulative inelastic energy loss during the surface collision. Kinetic energy is lost due to electron straggling (friction), as the ion approaches and leaves the surface, and due to electronic interactions that cause neutralization, excitation, and surface re-ionization of the incident projectile. Ion survival is unlikely at low incident energies, when contact time with the good metal surface is long, so re-ionization must occur to produce the detected N^+ exit. The first ionization energy of free N atoms is 14.53 eV,[18] which may be slightly reduced next to the surface due to the image charge effect, but should remain the dominant contribution to the large cumulative inelastic energy loss calculated from the linear plot of the exit energy vs. incident energy. Then, the intercept of this plot may serve as an upper bound for the surface re-ionization energy.

To further confirm the F adsorption effect on scattering dynamics, we have also performed O^+ scattering on Au. As in the case of N^+/Au, no scattered O^+ exit is detected when scattering off of clean Au: only a sputtering peak is seen for incident beam energies above 80 eV (Figure 3a). In contrast to N^+/Au, however, O^+/Au scatters exclusively as O^- (Figure 3b). Similar behavior has been observed in O^+/Cu(001) with primary energy below 1 keV.[8] The O^- exit energy is found to be a linear function of the incident O^+ beam energy with a slope of 0.8498, equal to the kinematic factor calculated from BCA for O^+/Au at a deflection angle of 90° (Figure 3c). The latter result confirms again that the observed O^- exit channel is from single collision events with individual Au atoms. The intercept of the linear fitting yields an inelastic energy loss of 7.97 eV associated with the formation of O^-.

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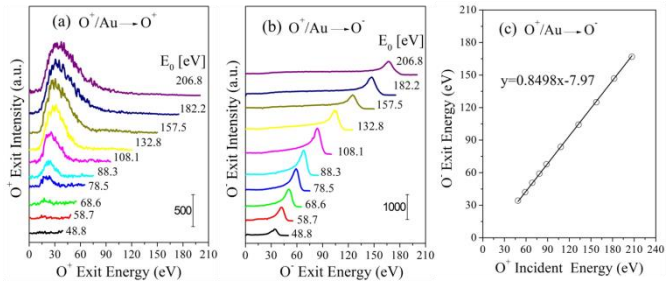

Figure 3. Energy distributions of (a) O^+ and (b) O^- ion exits from O^+ scattering on clean Au at various incident beam energies (E_0). O^- is the only scattered ion observed; only sputtered O^+ is observed at E_0 greater than ~70 eV. (c) Peak O^- exit energy as a function of incident O^+ beam energy. The linear fitting is performed with a fixed slope of 0.8498, corresponding to the BCA-calculated kinematic factor for O/Au at 90° deflection.

The energy and charge transfer dynamics during O^+ scattering on Au will be better understood if O^+ ion exits could also be detected simultaneously. As in the case of N^+/Au, adsorption of F atoms onto the Au surface allows the formation of positive ion exits. Figure 4 demonstrates the detection of both O^+ and O^- ion exits from O^+/Au at an incident beam energy of 88.3 eV, upon exposure of the surface to XeF_2 at a background pressure of 5×10^{-7} Torr. When the XeF_2 background pressure is increased to 5×10^{-6} Torr, the signal intensity of the O^+ exit increases (Figure 4a), while that of the O^- exit decreases (Figure 4b). Sputtering peaks are seen in both O^+ and O^- ion exit spectra, centered around 25 eV. The presence of F atoms on the surface was verified by a strong F^- sputtering peak, which behaved similarly to that seen for N^+/Au(XeF_2) (not shown).

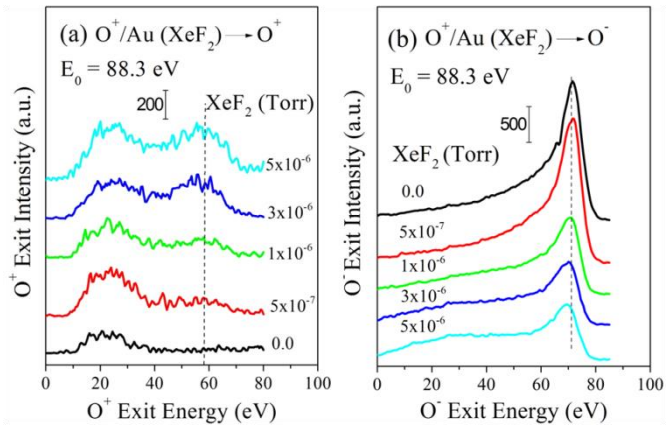

Figure 4. Energy distributions of (a) O^+ and (b) O^- ion exits for O^+ beam scattering on Au exposed to XeF_2 at various background pressures (E_0 = 88.3 eV). Inelastically scattered O^+ appears at ~58 eV only after exposure of the surface to XeF_2. O^+ signal intensity increases with background XeF_2 pressure. In contrast, O^- peak intensity decreases with background XeF_2 pressure.

Detailed scattering results for both O^- and O^+ exits as a function of the incident beam energy are shown in Figs. 5a and 5b, obtained at a XeF_2 pressure of 5×10^{-6} Torr. Both O^- and O^+ ion exit energies can be linearly fitted as a function of incident beam energy with the same kinematic factor of 0.8498 calculated from BCA, as shown in Figure 5c. The linear fittings, however, do not overlap. Instead, they exhibit different cumulative inelastic energy losses: 7.26 eV for O^- exits, and 15.45 eV for O^+ exits. Compared to scattering on clean Au (Figure 3c), the inelastic energy loss for O^- exits does not change much after F adsorption on Au (a difference of 0.7 eV). That is, in contrast to the scattering signal intensity of O^- exits, the energetics of O^- formation is not influenced significantly by the F adsorbate. This observation suggests that the electron capture process to form O^- from a neutralized atom is still occurring resonantly, albeit with a lower probability due to the stronger surface dipole.[8]

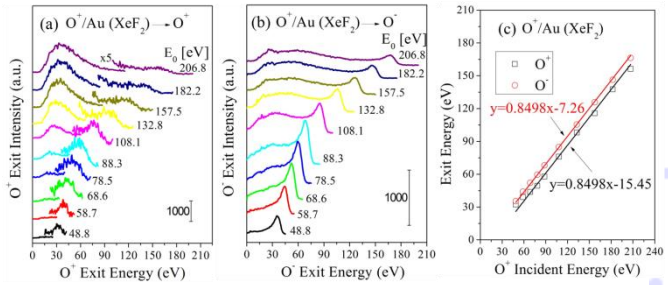

Figure 5. Energy distributions of (a) O^+ and (b) O^- ion exits from O^+ scattering on Au in a background of 5×10^{-6} Torr of XeF_2 at various incident beam energies (E_0).The O^+ scattered region in (a) is shown at a magnification of 5×. (c) O^+ and O^- ion exit energy plotted as a function of incident beam energy. The linear fittings are performed with a fixed slope of 0.8498, corresponding to the BCA-calculated kinematic factor for O/Au at a deflection angle of 90°. The O^- ion exit is 8.2 eV larger than the corresponding O^+ ion exit at the same incident energy.

The detection of both O^+ and O^- ion exits from O^+/Au provides more insight into surface re-ionization. First, the possibility of observing an O^+ exit from a surviving incident O^+ can be excluded. If that were to happen, the O^+ ion exit should suffer less energy loss than the corresponding O^- ion exit. The inelastic energy loss for O^+ exits is 15.45 eV (see Figure 5c), which is larger than the ionization energy of O atoms at 13.62 eV.[18] As suggested earlier in the case of N^+ exits, O^+ exits are probably formed by re-ionization of neutral O atoms during the hard collision.[8, 19] This is consistent with reports that reactive ions are completely neutralized in surface scattering.[20-21] In fact, it has been reported that there is no difference in scattered projectiles when comparing beams of O^- to beams of neutral O.[8, 19] Given a neutralized primary projectile, O^+ formation requires an outer-shell electron promotion during the hard collision at the expense of the atom kinetic energy. Once re-ionized during the hard collision, the detected O^+ ion yield depends mainly on the neutralization probability in the outgoing trajectory. Increasing surface work function should decrease this neutralization probability.[22] On the other hand, O^- formation may occur by resonant electron transfer from the Au metal surface to the affinity level of neutralized O. But in order to be detected in the gas phase, an O^- exit has to overcome a reaction barrier of ϕ-S, where ϕ is the metal surface work function and S is the electron affinity of the atom.[23] Polycrystalline Au has a work function of 5.1 eV, while the S of O is 1.46 eV. Therefore, an energy penalty of 3.6 eV is needed for O^- to escape the Au surface. This energy cost is 10 eV smaller than the ionization energy of O, which is within 20% of the experimentally observed difference of 8.2 eV between the inelastic energy loss for O^+ vs. O^- exits (Figure 5c). We deduce that the O^- exit possesses larger translational energy than that of the O^+ exit due to the lower energy penalty for resonant electron attachment vs. that for the re-ionization process.

Ion emission from surfaces bombarded by thermal atomic beams is described by the Saha-Langmuir equation,[10] which provides expressions for the positive (P^+) and negative (P^-) ion formation coefficient as follows:

$$P^+ = \frac{1}{1+\frac{g^0}{g^+}\exp\left(\frac{\phi - I}{kT}\right)} \qquad (1)$$

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$$P^- = \frac{1}{1+\frac{g^0}{g^-}\exp\left(-\frac{S-\phi}{kT}\right)} \quad (2)$$

where g^i the statistical weight of the relevant state, ϕ is the work function, I the ionization energy and S the electron affinity. Although these expressions are valid for ions emitted from the surface with an energy distribution determined by the surface temperature (i.e., under thermal equilibrium), they seem to capture the work function effect described herein. Eqn.(1), for example, predicts that a larger fraction of positive ions will be emitted by an increase in the work function of Au, consistent with the N^+/Au and O^+/Au experiments after surface fluorination. Likewise, Eqn.(2) captures the result for O^- exits, where the negative ion yield decreases with increasing surface work function. However, other effects may also be contributing at larger F coverages, such as atom shading reducing the Au surface area available for scattering.

In conclusion, we have demonstrated that the positive ion yield in energetic ion scattering on metal surfaces can be greatly enhanced by adsorbing electronegative species on the surface. Adsorption of F atoms on Au increases the surface work function thereby reducing the neutralization probability of exiting positive ions, formed in surface collisions. Whereas there is no scattering signal detected from N^+ ion scattering on clean Au, a pronounced N^+ scattering peak appears after exposing the Au surface to XeF_2. In scattering O^+ off of F-covered Au surfaces, both O^+ and O^- were observed. The inelastic energy loss of O^+ was larger than the ionization energy of O, which is consistent with the O^+ exit being produced by re-ionization of neutralized O species via an electron promotion. In contrast, the O^- ion is formed by resonant electron attachment and exits the surface with larger kinetic energy than O^+. Dosing the surface with electronegative adsorbates may be useful in the study of scattering dynamics of reactive ions at surfaces when the neutralization probability is high.

Experimental Section

All experiments were carried out in a custom-made ion scattering system, coupled to an ion beam-line.[24-26] Ions were extracted from an inductively-coupled plasma struck in Ar/N_2 or Ar/O_2 mixtures, collimated, and accelerated to 15kV to form a beam. Magnetic mass filtering produced a pure monoatomic beam (N^+ or O^+), which was then stripped of neutrals, decelerated, and delivered to a grounded target surface at an incident energy equal to the ion creation potential, which was controlled externally by a capacitive bias to the plasma. Both beams were delivered at the sample surface at an angle of incidence of 45° with respect to normal, and all products were detected at an angle of exit of 45° in the scattering plane. The beam current was measured on a grounded Au target and varied as a function of the incident energy between 2.0-2.4 μA for N^+ and between 12-16 μA for O^+ over a spot ~3mm in diameter. The Au target surface was cleaned using an Ar^+ ion gun before each experiment. Scattering products were mass- and energy-resolved using a quadrupole mass spectrometer and a 90°-sector electrostatic energy analyzer.

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Table of Contents

Surface Dynamics

Yunxi Yao and Konstantinos P. Giapis*

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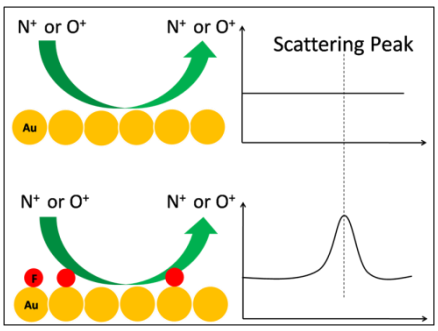
Tuning Charge Transfer in Ion-Surface Collisions at Hyperthermal Energies



Hunting the missing Ions: No positive ions are observed exiting in N^+ and O^+ ions scattered off on clean Au surfaces at hyperthermal energies. In situ partial adsorption of F atoms on the Au surface leads to the appearance of positively charged primary ions, a direct result of the increase in the Au work function.